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(54) Recovery of water and solids in a paper mill.

(57) There is disclosed a process for separating fine solids from water in the used water recovery system of a sheet forming mill, wherein the used water recovery system includes at least one stage in which an alkaline earth metal carbonate is precipitated in the aqueous suspension constituting the used water whereby the particulate material present in the used water becomes entrained in the alkaline earth metal carbonate precipitate. By the invention it is possible to recover the water and the fine solid materials which pass through the wire mesh belt of a paper or board forming machine, and optionally recycle those recovered materials.

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This inv ntion relates to an improved method for recov ring the wat r and th fine solid materials which pass through th wire mesh belt of a paper or board forming machin .

Sheet c llul sic products, for xampl paper and board, are g nerally manufactured on machines of the type in which a dilute susp nsion of finely divided solid materials in water is spread v nly over th surface of a moving wire mesh belt, which is generally referred to in the art as the "wire", and water is drawn through the wire by gravity and by suction to leave a thin felt-like mat of the solid materials on the wire. When the web of sheet material formed in this way is partially dewatered it is transferred from the wire to a moving felt band which provides it with support while further dewatering is carried out.

The solid material used in the formation of paper and board products generally consists predominantly of fibres which are most commonly of cellulose, but which may contain a proportion of synthetic fibres. The fibrous material may be prepared, for example, by subjecting wood to a series of mechanical and/or chemical processes which separate the fibres substantially one from another and make them available for the sheet forming process in lengths ranging from about 10μm to several millimetres. The solid material will often also include a particulate mineral material as a filler, the particles ranging in size from a fraction of a micrometer to about 50μm.

In order to manufacture a sheet material of homogeneous composition and uniform thickness, it is generally necessary to apply the solid material to the wire of the paper machine in the form of a very dilute aqueous suspension containing from about 0.5% to 1.0% by weight of solid material. This means that a very large quantity of water is required for the manufacture of paper and board; in fact the weight required is approximately two hundred times the weight of solid material used. It is therefore essential in most cases for environmental and economic reasons that as much as possible of the water which passes through the wire or is removed from the web of sheet material at a later stage is recovered for further use.

The water passing through the wire generally carries with it a substantial amount of fibrous or particulate material which is too fine to be retained by the mat of sheet material formed on the wire. This solid material is generally referred to as "fines". A useful definition of this term is given in the TAPPI Standard No. T 261 cm-90 "Fines fraction of paper stock by wet screening". This document describes a method for measuring the fines content of paper making stock or of pulp samples, and specifies that fines are those particles which will pass a round hole of diameter 76μm. Generally up to about 50% by weight of the solid material in the aqueous suspension which is fed to the head box of the sheet forming machine passes through the wire, and must be recovered for re-use. From about 1% to about 5% by weight of the solid material which is fed to a paper or board making process is finally rejected. Of this material, about 5% by weight is rejected because it is too coarse to be incorporated, and the remainder consists of fines.

The water which passes through the wire is generally referred to as "white water" on account of its high content of fine solids which gives it a high turbidity. Almost all of this white water is recirculated to the plant in which the paper making stock is prepared in what is called the "primary circulation loop". However, not all the white water can be recirculated in this way because less water is carried away from the sheet material forming machine in the moist web than is introduced with the new solid material. The excess white water is withdrawn from the primary circulation loop and is processed in a secondary circulation loop which separates as completely as possible the solid materials from the suspending water, so that the solid material can either be re-used in the stock preparation process, or discharged as waste. The water which is then substantially free of suspended solids can then either be re-used in the sheet material forming plant, for example in sprays or "showers", or as pump sealing water, in various parts of the process, or may be discharged to a convenient natural water course.

The secondary circulation loop makes use of various pieces of apparatus which are known generically as "save-alls". These generally operate on one of three principles, namely sedimentation, or filtration or flotation. In the sedimentation type of save-all the white water flows very slowly through a large tank so that the solid material sinks to the bottom and substantially clear water overflows at the top. It is usually necessary to add a chemical flocculant to the white water so that the solid material is present in the form of clusters of particles, rather than as discrete particles. Also the sedimentation type of save- all is rarely adequate on its own, but needs to be used in conjunction with additional separation equipment. The filtration type of save-all is operated by passing the white water through a filter medium, which may conveniently be a fine wire mesh, which is generally pre-coated with a layer of fibres to improve filtration. Again it is usually necessary to add a chemical flocculant to improve the separation of the solid particles from the water. In the flotation save-all process, the white water is introduced int a vessel in which a rising stream of fine air bubbles is provided. Th solid particles becom attached to th bubbles and ris to the surface where th y are skimmed off by rotating paddles. It is g nerally necessary to introduce a ch mical which rend rs th surface of th solid particles hydrophobic, and therefore increases their affinity with the air bubbles. It is usually necessary to use two or more save-alls in series to achiev acceptable separation of solid mat rial from the water.

According to the pres nt inventi n, there is provided a process for s parating fine solids from water in th used wat r recov ry system of a sheet f rming mill, wherein th us d wat r recovery system includes at least on stag in which an alkaline earth m tal carbonate is precipitated in th aqueous suspension constituting the us d water wh reby the particulat material pres nt in th us d wat r becomes ntrained in the alkalin earth metal carbonate precipitate.

The particulate material present in the used water will generally consist predominantly of "fines", in other words that material which, according to TAPPI Standard No. T 261 cm-90, will pass through a round hole of diameter 76μm.

The aqueous suspension constituting the used water will generally contain not more than about 5% by weight of particulate material, preferably not more than about 1% by weight of particulate material; such a dilute suspension of fine particles is difficult to separate into its solid and liquid components.

The suspension containing the precipitate of alkaline earth metal carbonate and entrained fine particulate material (or the separated filler itself) may be recycled to supplement the filler being used in the sheet forming process in the sheet forming mill. Alternatively, or in addition, the water separated from the suspension containing the precipitate of alkaline earth metal carbonate and entrained fine particulate material may be reused in the sheet forming mill.

In the process of the present invention, the alkaline earth metal carbonate precipitate may be formed by introducing into the suspension constituting the used water a source of alkaline earth metal ions and a source of carbonate ions. This will form the desired precipitate of alkaline earth metal carbonate <u>in situ</u> which will entrain the fine particles in the used water. The first reagent which is added is preferably uniformly distributed throughout the aqueous suspension to avoid local concentration gradients. When the first reagent is sparingly soluble, as is the case with calcium hydroxide, thorough mixing is desirable. It is also desirable that the suspension should be agitated while the second reagent is added in order to ensure an even distribution of the precipitate.

It is preferred to add the source of alkaline earth metal ions first followed by the source of carbonate ions. When the alkaline earth metal is calcium, this favours the precipitation of the scalenohedral form of calcium carbonate, which form appears to give the best light scattering properties when the aggregated product is to be re-used as a filler in the sheet forming process.

The source of alkaline earth metal ions is conveniently the alkaline earth metal hydroxide (known as milk of lime when the alkaline earth metal is calcium), but it may alternatively be a water-soluble alkaline earth metal salt, for example the chloride or nitrate. The alkaline earth metal hydroxide may be added already prepared to the aqueous suspension, or may be prepared in situ, for example by slaking an alkaline earth metal oxide (e.g. quicklime when the alkaline earth metal is calcium) in the suspension.

The source of carbonate ions is conveniently carbon dioxide gas which is introduced into the suspension containing the source of alkaline earth metal ions. The carbon dioxide gas may be substantially pure as supplied in gas cylinders or may be present as a mixture of gases such as flue or exhaust gases from a lime kiln or power plant. Alternatively, the source of carbonate ions may be an alkali metal or ammonium carbonate. Sodium carbonate is especially preferred on account of its relative cheapness and availability.

Whether the alkaline earth metal oxide is slaked in used water or in fresh water, the water may be at ambient temperature, but is preferably heated to a temperature in the range of from 30 to 50°C, and the suspension of the alkaline earth metal oxide in the water is preferably agitated vigorously for a time of up to 30 minutes to ensure that the slaking is complete.

When the alkaline earth metal is calcium and the source of carbonate ions is a carbon dioxide containing gas, the production of calcium carbonate in the scalenohedral form is favoured by maintaining the temperature of the mixture of used water and calcium hydroxide in the range of from 40 to 65°C. The carbon dioxide containing gas preferably contains from 5% to 50% by volume of carbon dioxide, the remainder being conveniently air or nitrogen.

The quantity of the source of alkaline earth metal ions and of the source of carbonate ions used is preferably such as to precipitate sufficient alkaline earth metal carbonate to give a weight ratio of alkaline earth metal carbonate to fine particulate material in the range from 1:99 to 90:10, more preferably 10:90 to 90:10. The suspension containing the precipitate of alkaline earth metal carbonate and entrained fine particulate material may be recycled directly in its relatively dilute form to supplement the filler being used in the sheet forming process. Alternatively the suspension containing the precipitate may be dewatered by any conventional method, for example by sedimentation, by pressure filtration, or in a centrifuge.

Th susp nsion of th precipitate of alkaline earth metal carbonate and ntrained fin particles is found to b very much easier to dewater than the original suspension of the fine particulate mat rial alone, because, when a cak of th precipitate is formed by filtration or by centrifuging, the packing of the particles is such that the cake is v ry much more p rmeable to water than is a cake formed from the solid component f th

used water alone. Also th precipitate, in many cases, is found to hav advantageous light scattering prop rties which mak it suitabl for use as a filler in a paper or board making process. Th precipitat may also find use as a fill r, for exampl , in polymeric compositions such as carpet backing compositions.

Th stage in which an alkalin earth metal carbonat is precipitated in th used water may conv niently replace either the first save-all stage or the second save-all stage of a conventional secondary circulation loop of a sheet forming process. Alternatively the alkaline earth metal carbonate precipitation stage may take as its feed suspension the solids fraction delivered by the second save-all stage.

The invention will now be illustrated, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is a flow diagram of a conventional secondary used water circulation system in a paper mill;

Figure 2 is a flow diagram showing a first mode in which the process of the invention may be carried out;

Figure 3 is a flow diagram showing a second mode in which the process of the invention may be carried out; and

Figure 4 is a flow diagram showing a third mode in which the process of the invention may be carried out.

In Figure 1, the reference numeral 1 represents the primary white water circulation system in a paper mill. An excess of used water passes through the wire of the paper making machine over that which can be returned as white water, and the excess used water overflows into a holding tank 2, whence it is transferred by means of a pump 3 and a conduits 4 to a first save-all 6, which may be, for example, of the sedimentation type. The solid particles which sink to the bottom of the save-all are returned in aqueous suspension through a conduit 8 to the primary circulation system. Water of reduced fine solids content overflows from the lip of the first save-all, but is insufficiently free of suspended solids to be used in the showers of the paper making process. This dilute suspension of fine particles is transferred by means of a pump 9 from the overflow lip of the first save-all to a second save-all 10, which may conveniently be of the type known as a clarifier which also operates on the sedimentation principle. Substantially clear water overflows from the second save-all and is returned through a conduit 11 to the primary circulation system. If required, clean water from the mains may be introduced through a conduit 12 to make up any deficiency in the quantity of water which is returned. A thickened sludge of fine particulate material is withdrawn from the base of the second save-all through a conduit 13 to an effluent treatment plant 14, in which the sludge is dewatered, for example by filtration, to give a cake of waste solid material which may be discharged at 15 to a suitable landfill site, and water of sufficiently good quality to be suitable for discharge through a conduit 16 to a natural water course.

Figure 2 shows a secondary used water circulation system in which the first save-all is replaced with a plant 17 in which, in accordance with the invention, an alkaline earth metal carbonate is precipitated in the aqueous suspension constituting the used water whereby the particulate material present in the used water becomes entrained in the alkaline earth metal carbonate precipitate. The mixture of aggregated solid material and water which is the product of the plant 17 passes through a conduit 18 to a dewatering device 19, which may conveniently be a vacuum disc filter. A cake of the aggregated solid material is withdrawn at 20 and may be transported to the stock preparation plant of the paper mill for incorporation as a filler in the paper mill stock, or may be used for some other purpose. Substantially clear water is returned by means of a pump 21 through a conduit 22 to the primary circulation system.

Figure 3 shows a secondary used water circulation system in which the second save-all is replaced with a plant 17 in which, in accordance with the invention, an alkaline earth metal carbonate is precipitated in the aqueous suspension constituting the used water. The mixture of aggregated solid material and water produced by the plant 17 passes through a conduit 18 to a vacuum disc filter 19. A cake of the aggregated solid material is formed and discharged at 20 for use as a filler in the paper mill stock, or for some other purpose. Substantially clear water is returned through a conduit 22 to the primary circulation system.

Figure 4 shows a secondary used water circulation system in which a plant 17 where, in accordance with the invention, an alkaline earth metal carbonate is precipitated in the aqueous suspension, is used to treat the solids sludge which is produced by the second save-all 10. The sludge passes to the plant 17 through a conduit 13, while substantially clear water is transferred by means of a pump 23 through a conduit 11 to the primary circulation system. The mixture of aggregated solid material and water produced by the plant 17 passes through a conduit 18 to a vacuum disc filter 19. A cake of the aggregated solid material is formed and discharged at 20 for use as a filler in the paper mill stock, or for some other purpose. Substantially clear water is returned by means of a pump 21 through a conduit 22 to the primary circulation system.

The invention is also illustrated by th f llowing examples.

EXAMPLE 1

Th used water entering th secondary circulati n system of a paper mill was found t contain 0.27% by

weight f suspend d solids which w re pred minantly cellulosic fibres, but also contained a smaller proportion of inorganic fill r particles. The first save-all of th s condary circulati n system was replaced, in th manner sh wn in Figure 2, with a plant in which th t mperatur of the used wat r was raised to 45°C, and th re was added thereto 56g of quicklime per litre of used wat r. Th resultant mixture was vigorously stirred until th slaking of the quicklime was complete. A gas containing 25% by volume of carbon dioxide, the remainder being air, was then admitted into the mixture, the temperature of the mixture being maintained at 45°C, at a rate sufficient to convert all the calcium hydroxide present into calcium carbonate. An aggregated crystalline precipitate was formed, and a sample of the aqueous suspension of this product, which resulted from the carbonation of the mixture of used water and hydrated lime, was tested for filtration rate by the method described in Appendix 1 below and was found to give a result of 6.1 units. By comparison, the filtration rate of the used water entering the secondary circulation system was found to be 0.0176 units. The process in accordance with the invention was therefore found to increase the rate of filtration of the used water by a factor of nearly 350.

The suspension of the aggregated precipitate was dewatered by means of a vacuum disc filter and the water separated in this way was found to be crystal clear with no detectable turbidity. Also the cake of the aggregated crystalline material was dried and was examined under a scanning electron microscope. It was found to consist of fine scalenohedral precipitated calcium carbonate in conjunction with the particles and fibres which were originally present in the used water.

EXAMPLE 2

The used water entering the secondary circulation system of a paper mill was found to contain 0.3% by weight of fine solid material, 80% by weight of which consisted of fine cellulosic fibres, the remainder being fine calcium carbonate filler particles. The first save-all of the secondary circulation system was replaced, in the manner shown in Figure 2, with a plant in which there was added to the used water at ambient temperature 134ml of an aqueous suspension of hydrated lime (calcium hydroxide) per litre of used water. The suspension of hydrated lime was prepared by slaking 112g of quicklime in 1 litre of water at 50°C with vigorous agitation for 25 minutes. Assuming that the quicklime is completely slaked, each litre of the suspension prepared in this way will contain 148g of calcium hydroxide. The weight of calcium hydroxide added per litre of used water was therefore 19.8g. A gas containing 25% by volume of carbon dioxide, the remainder being air, was then admitted into the mixture, the temperature of the mixture being maintained at 45°C, at a rate sufficient to convert all the calcium hydroxide present into calcium carbonate. An aggregated crystalline precipitate was formed, and a sample of the aqueous suspension of this product, which resulted from the carbonation of the mixture of used water and hydrated lime, was tested for filtration rate by the method described in Appendix 1 below and was found to give a result of 2.43 units. By comparison, the filtration rate of the used water entering the secondary circulation system was found to be 0.0048 units. The process in accordance with the invention was therefore found to increase the rate of filtration of the used water by a factor of over 500.

The suspension of the aggregated precipitate was dewatered by means of a vacuum disc filter and the water separated in this way was found to be crystal clear with no detectable turbidity. Also the cake of the aggregated crystalline material was dried and was examined under a scanning electron microscope. It was found to consist of fine scalenohedral precipitated calcium carbonate in conjunction with the particles and fibres which were originally present in the used water. This aggregated material was found to be very suitable for incorporation into the paper making stock as a filler.

Appendix 1

Filtration rate measurement method

A small sample of the suspension of the mixed mineral produced was poured into a Buchner filter funnel provided with a piece of standard filter paper, the side arm of the filtrate flask being connected to the laboratory vacuum source. The filtrate was collected in a measuring cylinder inside the filtrate flask, and at intervals the volume of filtrate collected and the time which had elapsed since the start of filtration were recorded. The square of the volume collected was plotted graphically against the elapsed time, and a curve was obtained which had a large central straight line portion. The slope of this straight line portion was recorded in each case.

The relationship between the square of the volume of filtrate collected and the elapsed time is given by the Carmen-Kozeny equation:-

$$\frac{Q^2}{T} = \frac{2.A^2.P.E^3.(y - 1)}{5.v.S^2.(1 - E^2).d^2}$$

where:

Q is the volume of filtrate collected;

T is the elapsed filtration time;

A is the area of the filter medium;

P is the differential pressure across the filter medium;

E is the fraction of voidage in the filter cake;

v is the viscosity of the suspending medium;

S is the specific surface area of the particulate phase; and

d is the specific gravity of the particulate phase.

The slope Q^2/T of the straight line portion of the graph plotted for each suspension gives a measure of the filtration rate in each case and, since A, P, v, S

and d can be assumed to be constant under the conditions of the experiment, a standardised filtration rate F can be found to be given by:

$$F = \frac{Q^2 . R}{T}$$

where:

$$R = \frac{\frac{1}{d} + \frac{W_C}{S_C}}{\frac{W_S}{S_S} - \frac{W_C}{S_C}}$$

where:

W_C is the weight fraction of water in the cake;

S_C is the weight fraction of solids in the cake;

W_S is the weight fraction of water in the suspension; and

S_S is the weight fraction of solids in the suspension.

Claims

1. A process for separating fine solids from water in the used water recovery system of a sheet forming mill, wherein the used water recovery system includes at least one stage in which an alkaline earth metal carbonate is precipitated in the aqueous suspension constituting the used water whereby the particulate material present in the used water becomes entrained in the alkaline earth metal carbonate precipitate.

2. A process according to claim 1, wherein the aqueous suspension constituting the used water contains not more than about 5% by weight of particulate material.

3. A process according to claim 1, wherein the aqueous suspension constituting the used water contains not more than about 1% by weight of particulate material.

4. A process according to claim 1, 2 or 3, wherein the alkaline earth metal carbonate precipitate is formed by introducing into the suspension constituting the used water a source of alkaline earth metal ions and a source of carbonate ions.

5. A process according to claim 4, wherein the alkaline earth metal is calcium.

6. A process according to claim 4 or 5, wherein the source of alkaline earth metal ions is added to the aqueous suspension first followed by the source of carbonate ions.

7. A process according to claim 4, 5 or 6, wherein the source of alkaline earth metal ions is an alkaline earth metal hydroxid or a water-soluble alkaline arth m tal salt.

8. A process according to claim 7, wherein the source of alkalin arth metal ions is th alkalin earth metal hydroxide which is added ready prepared to the aqu us suspension.

9. A process according t claim 7, wherein th source of alkalin earth metal ions is th alkalin earth metal hydroxid which is prepared in situ.

10. A process according to any on or more of claims 4 to 9, wherein th source of carbonate ions is carbon dioxide gas which is introduced into th susp nsion containing the source of alkalin arth metal ions.

11. A process according to any one or more of claims 4 to 9, wherein the source of carbonate ions is an alkali metal or ammonium carbonate.

12. A process according to claim 10, in which the source of alkaline earth metal ions is an alkaline earth metal hydroxide and the source of carbonate ions is a carbon dioxide containing gas, wherein the production of calcium carbonate in the scalenohedral form is favoured by maintaining the temperature of the mixture of used water and calcium hydroxide in the range of from 40 to 65°C.

13. A process according to claim 10 or 12, wherein the carbon dioxide containing gas preferably contains from 5% to 50% by volume of carbon dioxide.

14. A process according to any one of claims 4 to 13, wherein the quantity of the source of alkaline earth metal ions and of the source of carbonate ions used is such as to precipitate sufficient alkaline earth metal carbonate to give a weight ratio of alkaline earth metal carbonate to fine particulate material in the range from 1:99 to 90:10.

15. A process according to any one or more of the preceding claims, wherein the suspension containing the precipitate of alkaline earth metal carbonate and entrained fine particulate material is recycled to supplement the filler being used in the sheet forming process.

16. A process according to any one or more of the preceding claims, wherein the precipitate of alkaline earth metal carbonate and entrained fine particulate material is separated from the suspension thereof and the precipitate is recycled to the sheet forming process.

17. A process according to any one or more of the preceding claims, wherein water separated from the suspension containing the precipitate of alkaline earth metal carbonate and entrained fine particulate material is reused in the sheet forming mill.

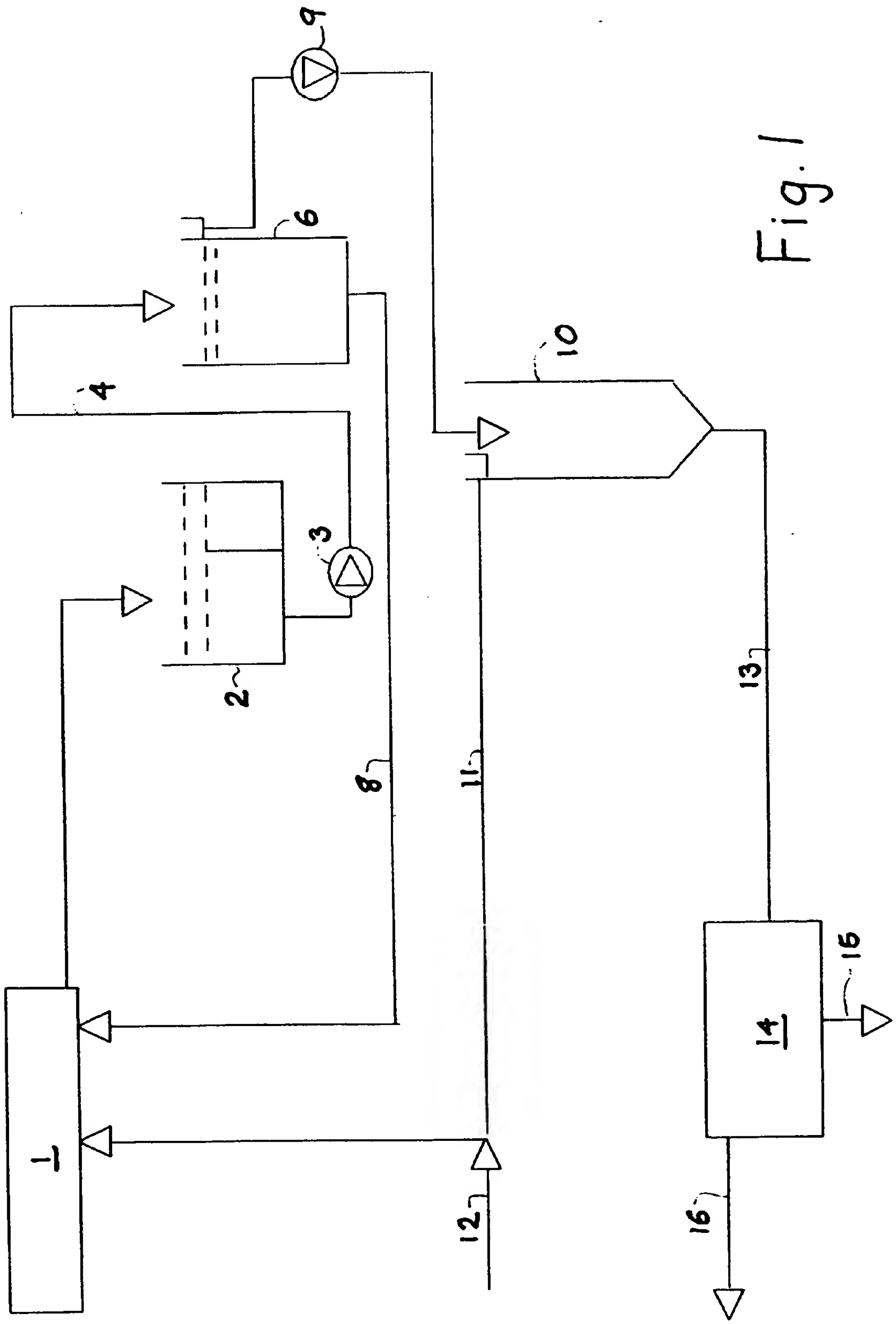

Fig. 1

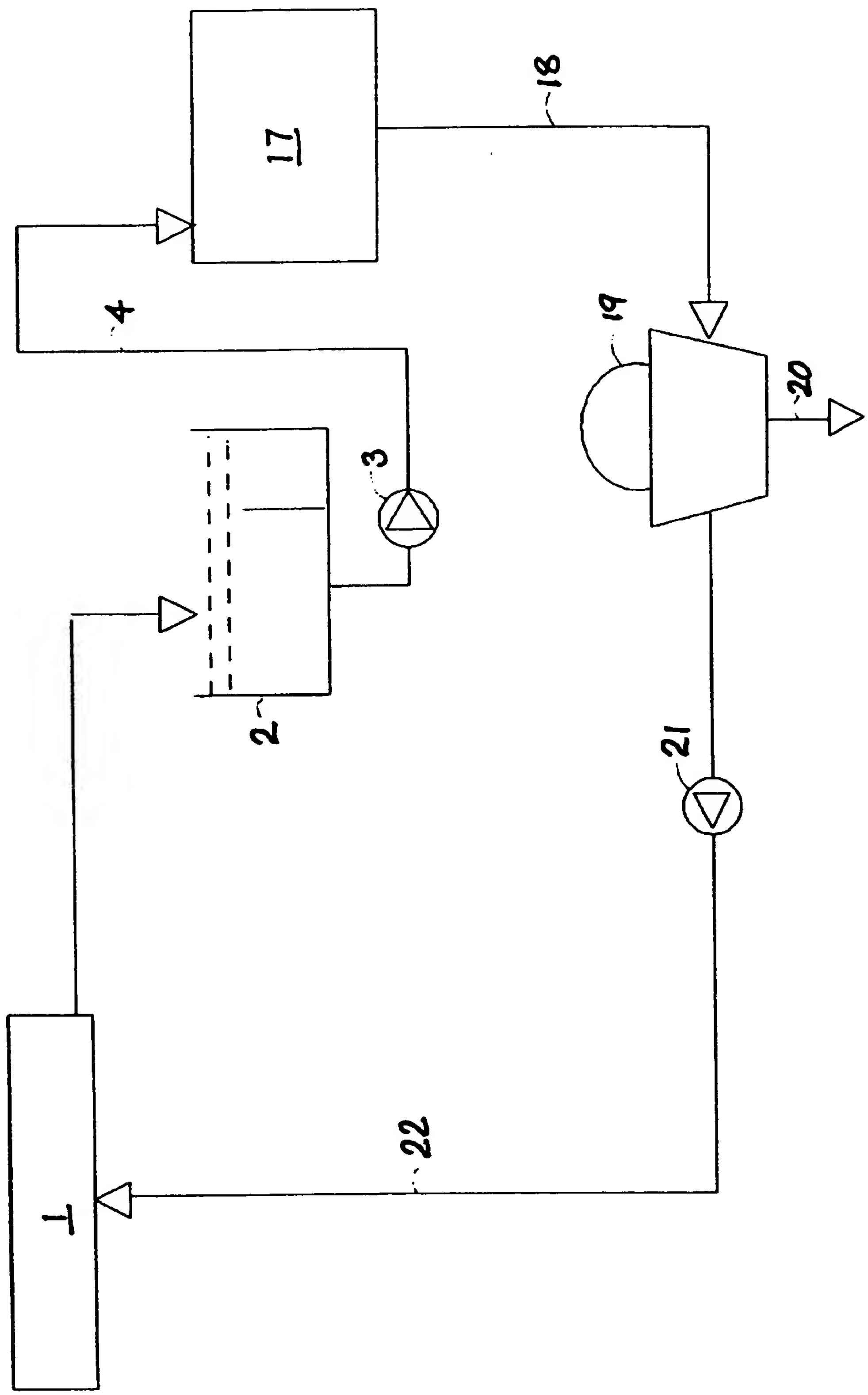

Fig. 2

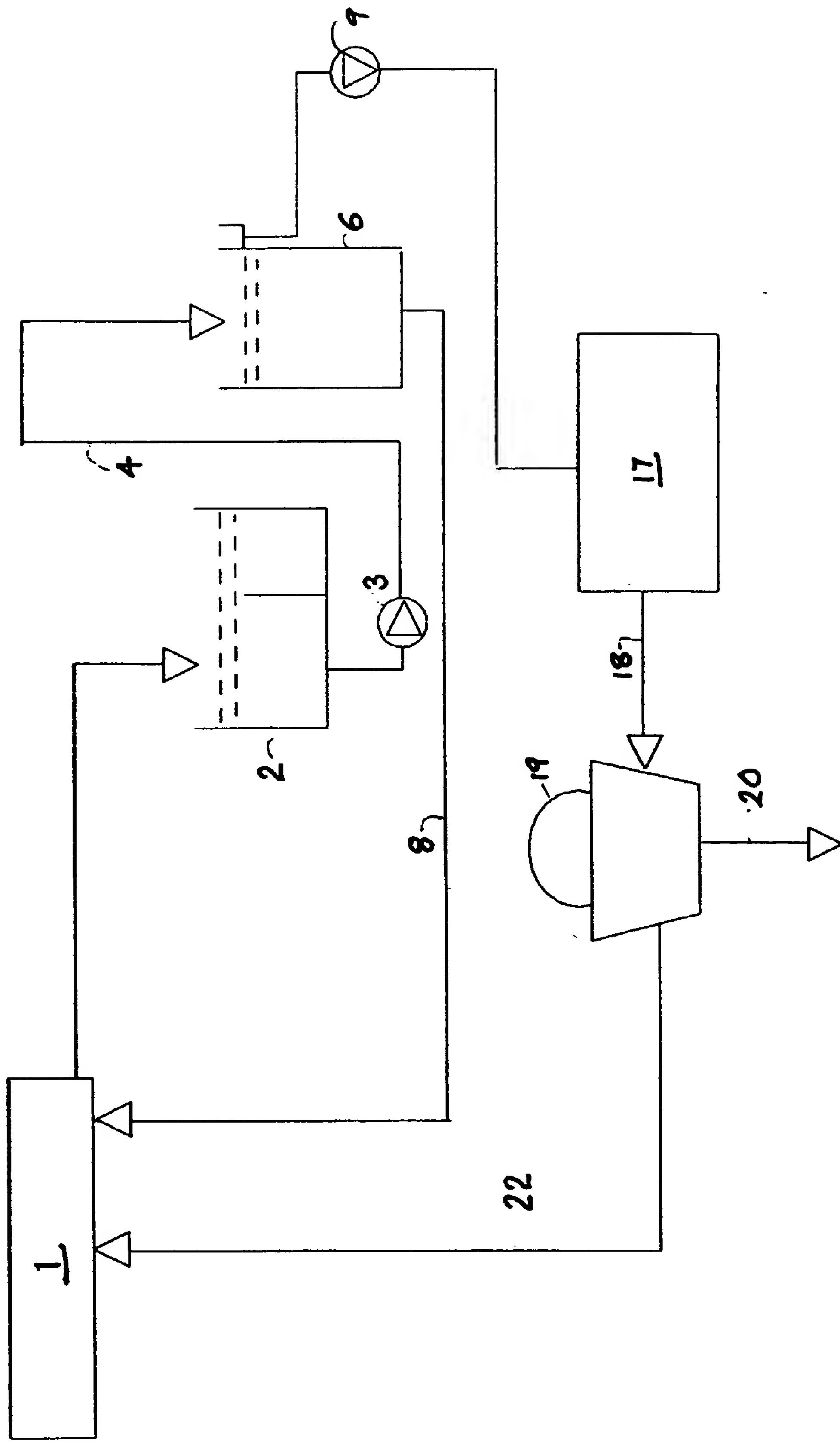

Fig. 3

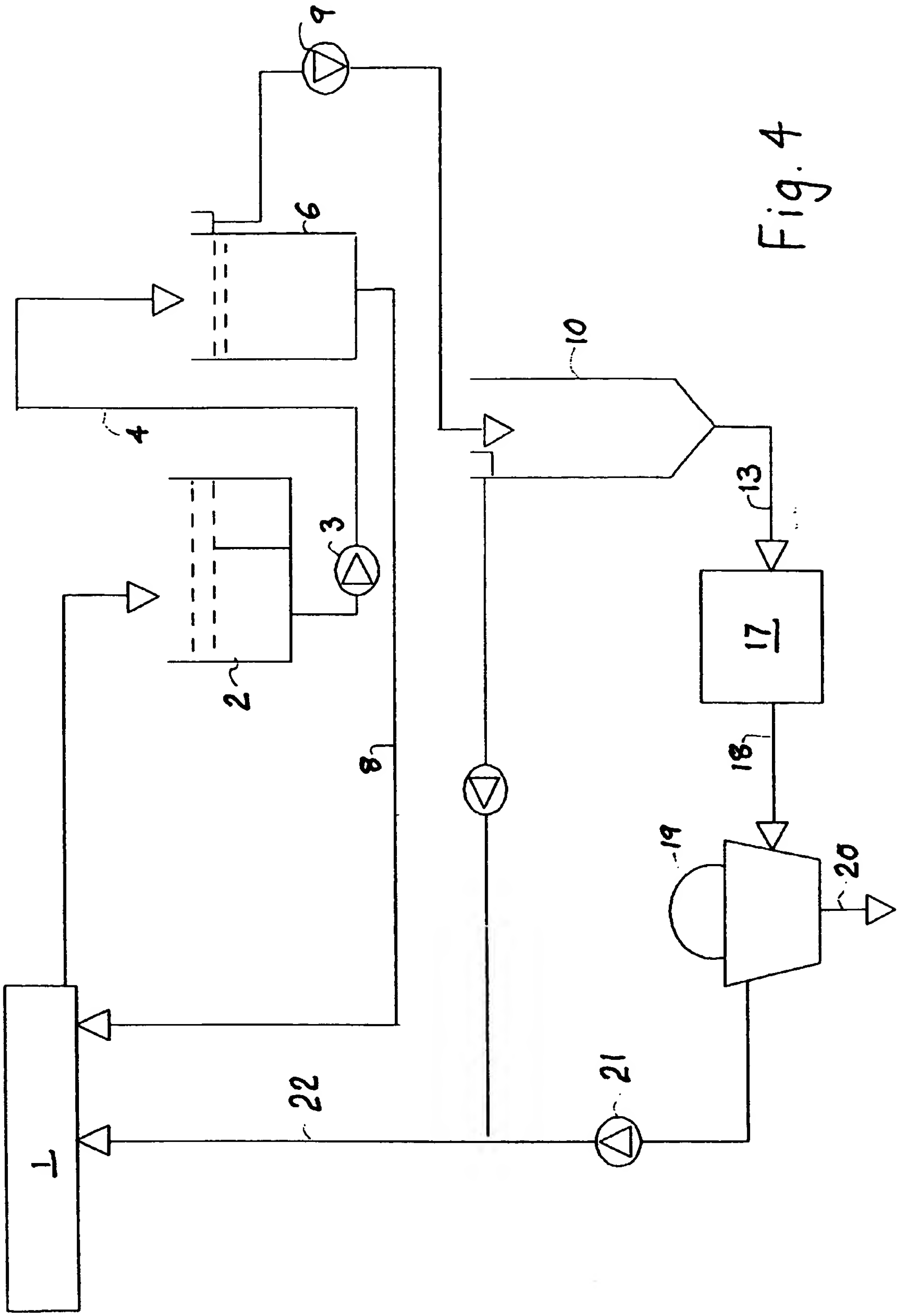

Fig. 4

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EUROPEAN SEARCH REPORT

Application Number
EP 94 30 4437

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
A	US-A-3 152 001 (PODSCHUS ET AL.) * the whole document * ---	1-17	C09C1/00 D21H17/69 D21H19/38
A	US-A-2 470 577 (RODERICK ET AL.) * the whole document * -----	1-17	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)
			D21H C09C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	27 January 1995	Songy, O

CATEGORY OF CITED DOCUMENTS

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